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Studies of the Structure and Properties of Amorphous $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$

R. C. BOWMAN, JR.
Chemistry and Physics Laboratory
The Aerospace Corporation
El Segundo, CA 90245

A. J. MAELAND
Allied/Signal Corporation
Morristown, NJ 07960

K. M. UNRUH
Department of Physics
University of Delaware
Newark, DE 19716

E. L. VENTURINI
Sandia National Laboratories
Albuquerque, NM 87185

J. J. RUSH
National Bureau of Standards
Gaithersburg, MD 20899

J. S. CANTRELL
Chemistry Department
Miami University
Oxford, OH 45056

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AIR FORCE SPACE TECHNOLOGY CENTER
Kirtland Air Force Base, NM 87117

SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
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Los Angeles, CA 90009-2960

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ samples with $x \leq 173$ have been shown to remain amorphous after reaction of the glassy alloy with gaseous hydrogen. Magnetic susceptibility and Mössbauer spectroscopy indicate that the electronic structure of the alloy is modified upon hydrogen absorption. Proton spin-lattice relaxation times suggest a strong hyperfine interaction with the iron d-states. The vibrational spectrum of $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{173}$ from inelastic neutron scattering shows hydrogen occupancy in a distribution of tetrahedral interstitial sites. Calorimetry and x-ray diffraction demonstrate that $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ with $x > 140$ irreversibly crystallizes into $c\text{-ZrH}_x$ and ZrFe_2 .					
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PREFACE

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During the past decade, the formation of amorphous hydrides from glassy or crystalline alloys has been widely studied.¹ Since the Zr-based metallic glasses can often absorb large quantities of hydrogen without crystallization, the properties of these amorphous hydrides are especially interesting.²⁻⁵ Fries, et al.^{6, 7} have studied several glassy $a\text{-Zr}_{1-y}\text{Fe}_y$ alloys before and after electrolytic charging with hydrogen. They reported an unusually large hydrogen absorption for the $y = 0.24$ glass—namely, the nominal maximum composition $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{246}$. The present work describes evaluations of $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ samples prepared by reacting the glassy alloy with hydrogen gas.

The $a\text{-Zr}_{76}\text{Fe}_{24}$ glass was produced by conventional melt-spinning. X-ray diffraction (XRD) did not show any crystalline components in these ribbons, and the alloy density was found to be $6.81(2) \text{ g/cm}^3$. The alloy was reacted at room temperature with hydrogen gas where the initial pressures were slightly above one atmosphere. Thermal desorption measurements^{4,5} on the powdered product gave a saturated composition of $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{173}$. Figure 1 presents the XRD pattern from some of this hydrided material. There is no evidence of any crystalline phases, and the decrease in the peak position (i.e., at $2\Theta_p = 33.7^\circ$) relative to the value for the initial glass (i.e., $2\Theta_p = 36.3^\circ$) corresponds to a net volume expansion of $2.67\text{\AA}^3/\text{H-atom}$.

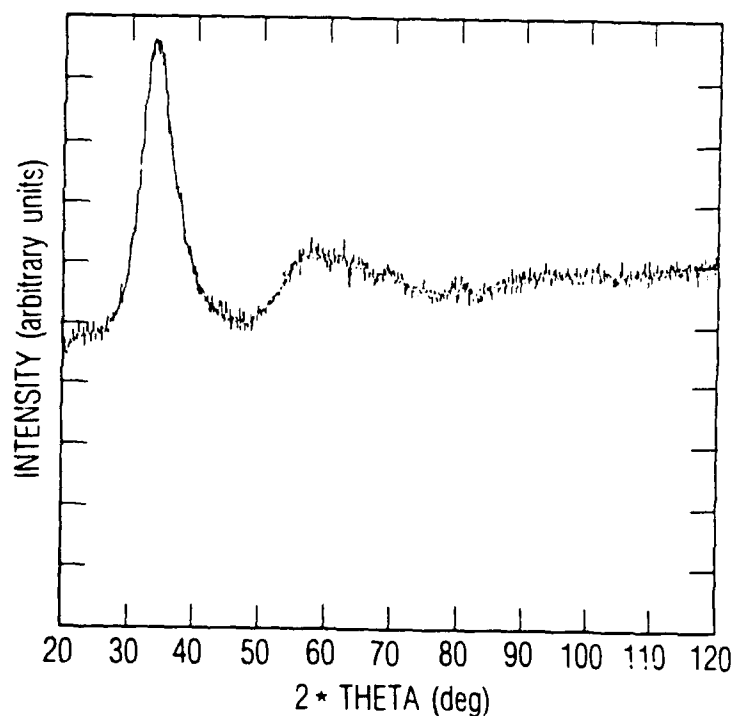


Fig 1. X-ray Diffraction Pattern for $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{173}$ Obtained with $\text{Cu K}\alpha$ Radiation.

In order to obtain insight into the hydrogen site occupancy, an inelastic neutron scattering (INS) study was made on $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{173}$; its room temperature vibrational spectrum is shown in Figure 2. The peak maximum is at 137(4) MeV, and the full-width half maximum is 63(6) MeV. These values are very close to the INS results for other amorphous Zr-based hydrides where hydrogen atoms predominantly occupy tetrahedral sites with mostly Zr neighbors.⁵ However, the large linewidths imply considerable distortions and possibly some occupancy of sites with different symmetries.⁵

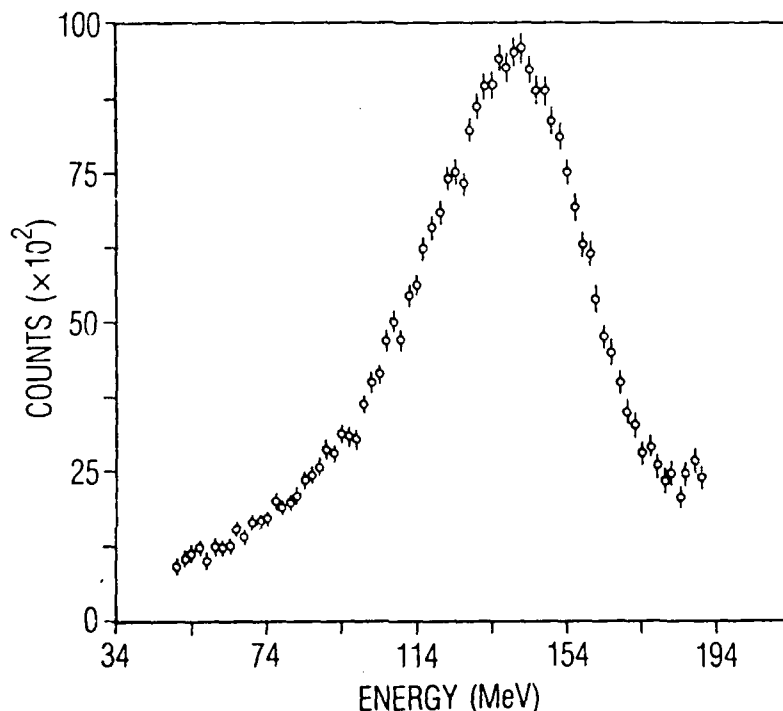


Fig 2. Hydrogen Vibration Spectrum for $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{173}$ from Inelastic Neutron Scattering Measurement at Room Temperature.

A previously described² SQUID magnetometer was used to determine magnetic properties between 7 K and 300 K for magnetic fields up to 40kOe. The magnetic susceptibilities $\chi(T)$ for three $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ samples are shown in Figure 3. The glassy alloy $a\text{-Zr}_{76}\text{Fe}_{24}$ exhibits Pauli paramagnetism with $\chi(T)$ being nearly temperature-independent, which contrasts with some past measurements.^{8,9} However, $\chi(T)$ curves for the amorphous hydrides show a Curie-Weiss term, which is most likely due to superparamagnetic Fe clusters or iron oxides produced by surface decomposition during hydriding. As shown in Table I, the Pauli terms $\chi(0)$ for the hydrides are equal or even 10% smaller than for the alloy.

Nuclear magnetic resonance (NMR) determinations of the proton spin-lattice relaxation times (T_1) have provided useful assessments of the electronic structures of many

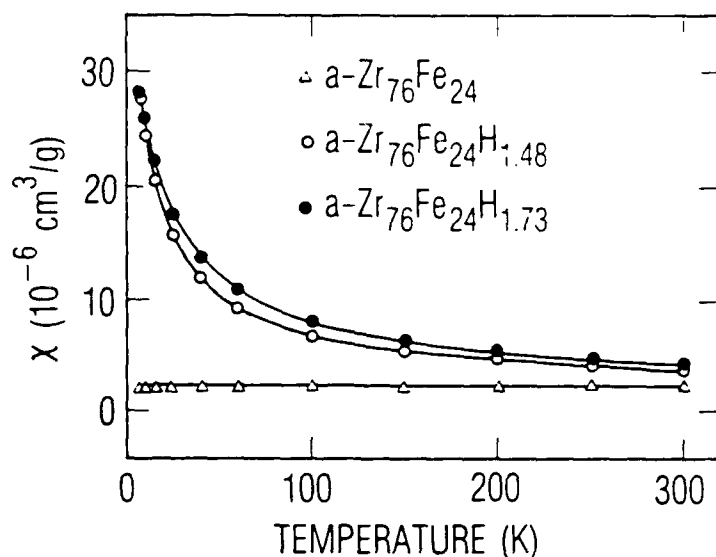


Fig. 3. Temperature Dependence of Magnetic Susceptibilities (χ) Where the Curves Are Least-square Fits with $\chi(T) = \chi(0)\{1 + BT\}$ for the Alloy and $\chi(T) = \chi(0) + C/T + \Theta$ for the Amorphous Hydrides.

Table I. Summary of Various Parameters from $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ Samples. See text for definitions.

x	$\chi(0)$ ($10^{-6}\text{cm}^3/\text{g}$)	\overline{IS} (mm/s)	\overline{QS} (mm/s)	$(T_1T)^{-1/2}$ ($\text{s} \cdot \text{K}$) $^{-1/2}$	T_{exo} (K)	T_{endo} (K)
0	2.27	-0.263	0.55	—	663,802	—
148	2.33	+0.270	0.49	0.64	541	552
173	1.99	+0.272	0.49	0.61	534	542

crystalline and amorphous hydrides.^{3, 5, 10, 11} Figure 4 summarizes the proton T_1 results obtained at 34.5 MHz on the two $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ samples. Table I contains the $(T_1T)^{-1/2}$ parameters [which are directly proportional to the density (N_F) of electronic states at the Fermi level].^{3, 10} When compared with values for other amorphous Zr-based hydrides,^{3, 5, 10} the $(T_1T)^{-1/2}$ data in Table I are nearly an order of magnitude larger. However, this differ-

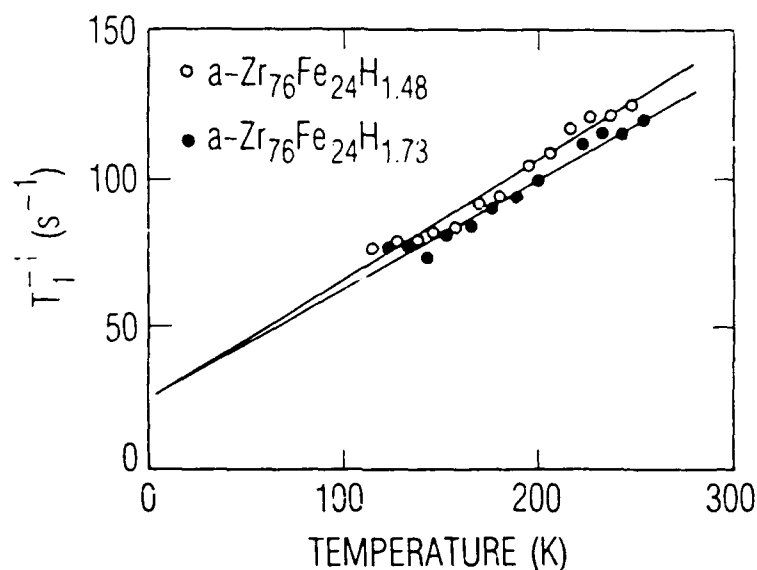


Fig. 4. Inverse Proton Spin-Lattice Relaxation Times Where the Korringa Parameters (T_1T) Are Derived from the Slopes of the Solid Lines.

ence is not believed to reflect an unusually large N_F but rather a very strong hyperfine interaction with the Fermi level iron d-states as was previously found in crystalline TiFeH_x .¹¹ Presumably, the electronic structure of $\text{a-Zr}_{76}\text{Fe}_{24}\text{H}_x$ has the iron states sufficiently near the Fermi level to influence the protons via a polarization mechanism.¹⁰

The Mössbauer spectra of the ^{57}Fe isotope were obtained at room temperature and at 4.2 K in conventional transmission geometry. Two 4.2 K spectra are shown in Figure 5, along with fits using the distributions of quadrupole splittings P (QS) obtained by a modification of Window's method.¹² Both $\text{a-Zr}_{76}\text{Fe}_{24}$ alloy and $\text{a-Zr}_{76}\text{Fe}_{24}\text{H}_{1.73}$ are paramagnetic at this temperature (as well as room temperature—see Fries, et al.^{6, 7}). Furthermore, there is no indication of ferromagnetic iron precipitates in these Mössbauer spectra. However, the suspected magnetic Fe clusters¹³ require the conversion electron Mössbauer technique for this direct detection. The mean isomer shifts (\bar{IS}) referred to $\alpha\text{-Fe}$ and quadrupole splittings (\bar{QS}) obtained at RT are presented in Table I. As reported by Fried, et al.^{6, 7} hydrogenation of $\text{a-Zr}_{76}\text{Fe}_{24}$ causes a substantial increase in \bar{IS} that probably reflects changes in electronic structure¹⁴ (e.g., a partial charge transfer from Fe to H) in addition to a contribution from the volume expansion. The quadrupole splitting distributions in Figure 5 indicate a significant increase in the near-zero range for the hydride, suggesting some structural changes to give iron symmetries that are more nearly cubic⁶ than in the original glassy alloy.

The thermal stabilities of $\text{a-Zr}_{76}\text{Fe}_{24}\text{H}_x$ have been studied by differential scanning calorimetry (DSC) and XRD after quenching from different temperatures.^{4, 5} Representative

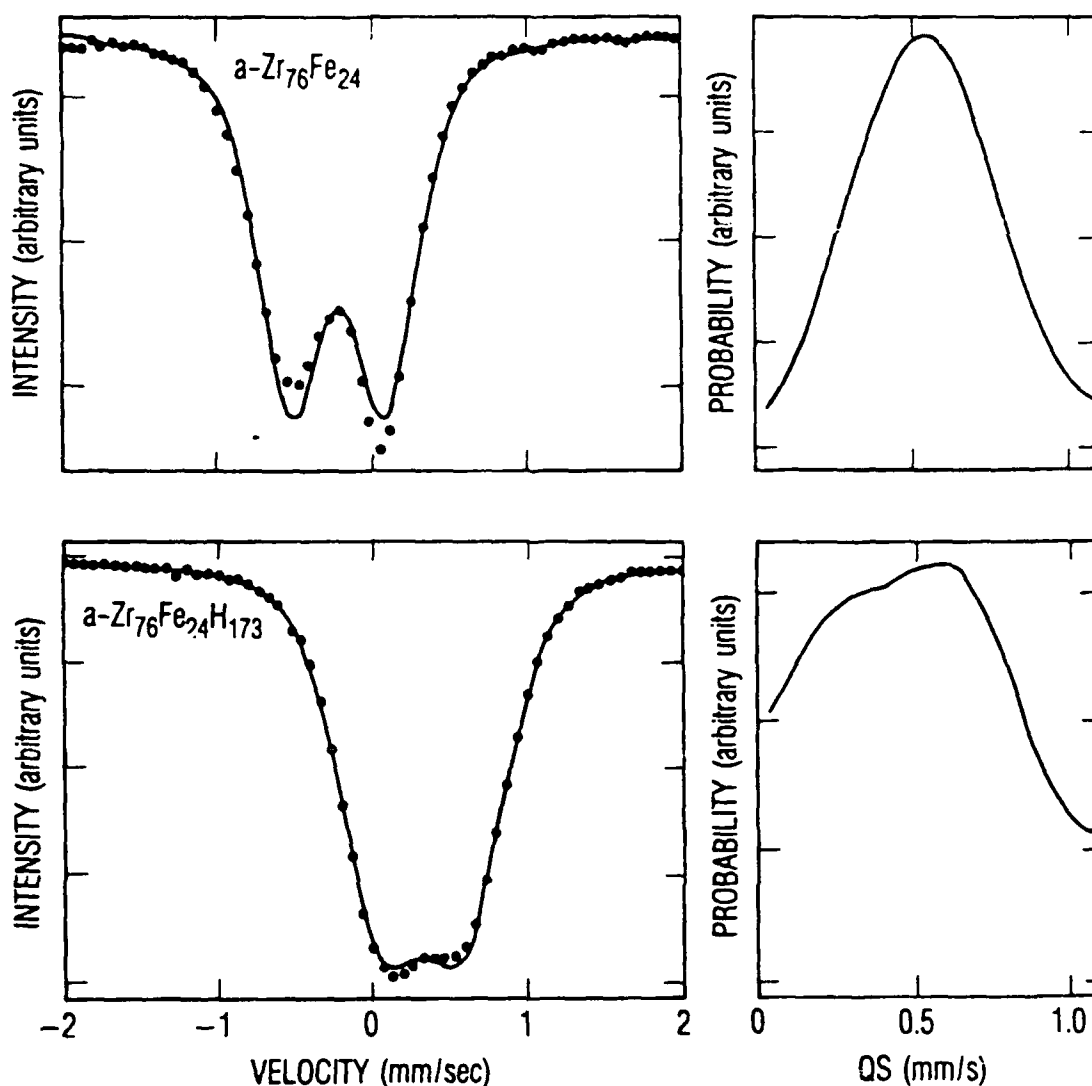


Fig 5. Mössbauer Spectra for Two $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ Samples Obtained at 4.2 K. The solid curves are fits through the data with the distributions of quadrupole splittings $P(QS)$ shown on the right side.

DSC curves are presented in Figure 6, where the exothermic peaks (T_{exo}) indicate crystallization or phase transitions^{4,5} and the endothermic peak (T_{endo}) corresponds to hydrogen evolution.^{4,5} The peak temperatures are summarized in Table I. From the XRD results, the alloy $a\text{-Zr}_{76}\text{Fe}_{24}$ initially crystallizes at 663 K to form hexagonal $\omega\text{-Zr}$ and cubic Zr_2Fe but subsequently transforms into orthorhombic Zr_3Fe above 802 K. Additional information on $a\text{-Zr}_{1-y}\text{Fe}_y$ crystallization is given by Cantrell and Bowman⁴ and Matsuura.¹⁵ The DSC measurements show that $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ crystallizes at a much lower temperature than the alloy. Furthermore, XRD indicated that ZrH_x formed during crystallization with a complementary intermetallic phase ZrFe_2 for the highest quench temperature. Our results differ

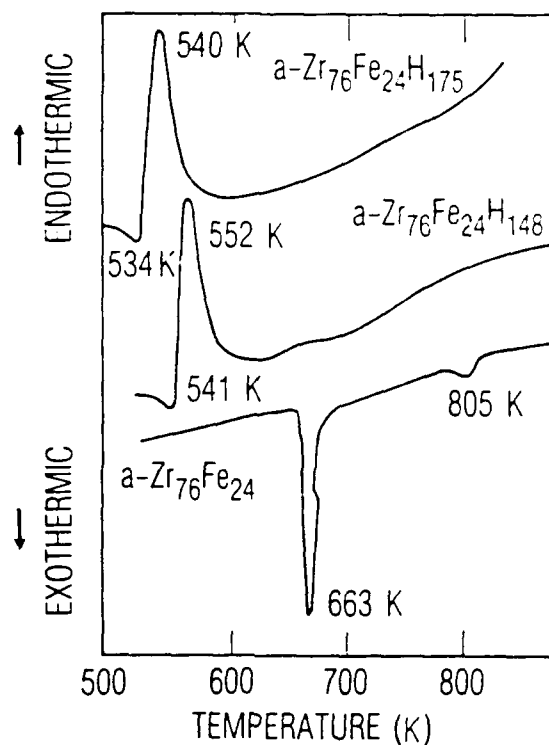


Fig. 6. DSC Traces for Heating Rates of 20 K/min.

from those for electrolytically charged $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_{220}$,⁶ where no ZrH_x or ZrFe_2 was detected but the ternary oxide Zr_2FeO_x was found instead. Electrolytic charging probably introduced sufficient oxygen impurities to alter the phases formed during crystallization and inhibited the endothermic loss of hydrogen seen in Figure 6 from the $a\text{-Zr}_{76}\text{Fe}_{24}\text{H}_x$ samples produced with hydrogen gas. It is noteworthy that these latter samples yielded ZrH_x as the major decomposition product, which was found when several other Zr-based amorphous hydrides^{4, 5} underwent crystallization.

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